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Marangoni enhancement of desulphurization of liquid iron

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Liquid iron at $1600 \,^{\circ}$ C, containing $0.088 \,\text{wt\%}$ S and $0.070 \,\text{wt\%}$ O, was desulphurized by a lime-saturated calcium ferrite slag at a rate significantly greater than that calculated on the assumption that diffusion of sulphur in the liquid iron was rate controlling. It is postulated that the transfer of sulphur across the slag-metal interface caused local variations in the interfacial energy, which induced Marangoni stirring in both the metal and slag phases.

Keywords: desulphurization; liquid iron; lime-saturated calcium ferrite slag; kinetics; Marangoni stirring; turbulence

1. Introduction

When placed in a slip-cast lime crucible at $1600 \,^{\circ}$ C, liquid irons containing 1.62 and 0.66 wt% sulphur, were desulphurized by the crucible. Reaction between the crucible and sulphur in the iron produces a liquid which rapidly penetrates the wall of the crucible. The assumption that the rate of desulphurization of the melt was controlled by diffusion of sulphur in the iron gave a diffusion coefficient of $6.7 \pm 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which is in good agreement with the values of 4.86×10^{-5} and 4.63×10^{-5} cm² s⁻¹ measured at 1600 °C, respectively, by Kawai (1956) and Majdic et al. (1969) using conventional experimental techniques. It was found that liquid iron containing 0.088 wt% sulphur was not desulphurized by the crucible, presumably because the activity of iron sulphide in this melt was not high enough to cause reaction with the lime crucible. However, when brought into contact with lime-saturated liquid iron oxide (of composition 58% FeO-42% CaO) at 1600 °C, the melt was desulphurized at a rate significantly higher than that calculated on the assumption of control by diffusion of sulphur in the liquid iron. For example, with a fixed geometry of a slag-metal interfacial area of 1.5 cm^2 and a mass of iron melt of 5 g, the measured sulphur content of the iron decreased from 0.08 to 0.02 wt% in 4 min in comparison with a decrease from 0.08 to 0.065 wt% in 4 min calculated assuming diffusion control in the liquid iron. The addition of 4 wt% CaF₂ to the lime-saturated oxide melt had no influence on the rate of desulphurization of the iron. It is postulated that this enhanced rate of desulphurization is caused by Marangoni turbulence at the slag-metal interface and the following is an application, to the experimental system, of the two fundamentally differing forms of the Marangoni effect given by Berg (1982). The transfer of sulphur from metal to slag causes a decrease in the interfacial tension and, in the first type of effect, any local variation in the interfacial tension causes a disturbance in the form of a dilation, as illustrated in figure 1a. This dilation, in turn, brings solute-rich metal to the site of the dilation which further decreases the surface tension and sets

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 955

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Figure 1. Schematic representations of (a) the first form of the Marangoni effect and (b) the second form of the Marangoni effect (adapted from Berg (1982)).



Figure 2. Illustration of the growth of a 'head' on the iron ingot with time caused by dissolution of the CaO crucible along its line of contact with the slag-metal interface. Desulphurization times increase in passing from the ingot on the left to the ingot on the right.

up forces which promote further dilation until macroscopic convection is generated. In the second type of effect, the transfer of sulphur upward from the interface preferentially depletes a narrow region beneath the meniscus near the crucible wall, which causes a higher interfacial tension near the wall. This propels the interface toward the wall and sets up the circulation in the bulk phase shown in figure 1b. Evidence for the latter effect was provided by the observation of the growth of a 'head' on the metal ingot during desulphurization. This growth is shown in figure 2, in which the reaction time increases from left to right. The enrichment, in iron and sulphur, of the slag being circulated at the wall undersaturates the slag with respect to CaO and hence causes dissolution of the crucible along its line of contact with the slag and metal.

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Phil. Trans. R. Soc. Lond. A (1998)

956